

# Ion Hydration and Associated Defects in Hydrogen Bond Network of Water: Observation of Reorientationally Slow Waters beyond First Hydration Shell

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Effects of presence of ions, at moderate to high concentrations, on dynamical properties of water molecules are investigated through molecular dynamics simulations. Simulations reveal that the presence of magnesium chloride ( $\text{MgCl}_2$ ) induces perturbations in the hydrogen bond network of water leading to the formation of bulk-like domains with ‘defect sites’ on boundaries of such domains: water molecules at such defect sites have less number of hydrogen bonds than those in bulk water. Reorientational autocorrelation functions for dipole vectors of such defect water molecules are computed at different concentrations of ions and compared with system of pure water. Earlier experimental and simulation studies indicate significant differences in reorientational dynamics for water molecules in the first hydration shell of many dissolved ions. Results of this study suggest that defect water molecules, which are beyond the first hydration shells of ions, also experience significant slowing down of reorientation times as a function of concentration in the case of  $\text{MgCl}_2$ . However, addition of cesium chloride ( $\text{CsCl}$ ) to water does not perturb the hydrogen bond network of water significantly even at higher concentrations. This difference in behavior between  $\text{MgCl}_2$  and  $\text{CsCl}$  is consistent with the well-known Hofmeister series.

*Introduction*— Effects of simple inorganic salts on the molecular properties of water are at the heart of a vast number of interesting and complex processes such as the stability of proteins and nucleic acids [1] and environmentally relevant processes [2, 3]. Understanding the effect of dissolved ions on the structural and dynamical properties of water is essential in this regard. The Hofmeister effect, which includes highly ion-specific effects on aggregation dynamics of proteins [4, 5] and other biologically relevant processes [5–7] has been of significant interest lately. Spectroscopic techniques have been instrumental in probing the cooperative ion hydration mechanism and consequent long-range structural and dynamical effects of certain salts, or ion combinations, on water [8–14]. Earlier experiments suggested that the effect of ions on dynamical properties of water is largely restricted to their first hydration shell [15, 16]. However, recent experiments, using a combination of femtosecond time resolved infrared (fs-IR) and dielectric relaxation spectroscopy, have shown the existence of a fraction of reorientationally slow waters [8, 9] well beyond the first hydration shells of dissolved  $\text{MgSO}_4$  ions. In these experiments, two sub-populations of waters were identified for various salts: one with reorientation timescales comparable to pure water ( $\sim 2.6$  ps) and the other showing characteristically slower reorientations ( $\sim 10$  ps). The fraction of total water molecules contributing to the sub-population of slow-waters was seen to increase with increase in salt concentration for all salts and the magnitude of increase was observed to be highly dependent on ion combinations: being largest for combinations of strongly hydrated ion species ( $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ).

Despite the recent experimental results [8], the existence of long-range effects of salts, beyond first hydration shell, is controversial owing to results from other experimental [15–18] as well as simulation [17, 19–22] studies which suggest the contrary. While an intense cooperative slowdown of water reorientation has been observed in presence of ions with high charge densities, the range of presence of slow waters has been found to be confined to the first hydration shell of the ions [16, 17, 19–22]. The focus of present work is on the extended hydrogen bond network in bulk water and the domain formation and existence of ‘defect water molecules’ at boundaries of such domains, when salt is added. Instead of classifying water molecules based on radially varying spherical hydration shells around ions, sub-populations depending on whether they are bulk-like or defect water molecules are considered. Using molecular dynamics (MD) simulations, we present evidence for reorientational slowdown of water well beyond the first hydration shell for solutions of  $\text{MgCl}_2$  and effect of salt concentration of the same. However for  $\text{CsCl}$ -water solutions, no significant effect on reorientational dynamics of water (irrespective of  $\text{CsCl}$  concentration) was found, which is in good agreement with the Hofmeister series.

*System setup*— All simulations were performed with TIP3P [23] water model and using simulation package NAMD 2.9 [24]. Standard CHARMM parameters were used for ions [25]. Initially a  $50\text{\AA} \times 50\text{\AA} \times 50\text{\AA}$  box of water containing 4972 water molecules was equilibrated for 10 ns. *Solvate* plugin of VMD [26] was used to produce  $\text{MgCl}_2$  (2M, 3M, 4M) and  $\text{CsCl}$  (3M, 4M) solutions from this equilibrated configuration and each of the salt-water systems was equilibrated for 14 ns. The pure water system was further simulated for 4 ns, resulting in a 14 ns equilibration simulations for each of the six systems considered. Further details of system setup are included in the TABLE SI of Supplementary Informa-

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tion (*Supp. Info.*). Relatively high salt concentrations of salt were chosen in this study based on recently studied experimental concentrations [9, 18] as well as for good statistics. For computation of reorientational autocorrelation functions and other dynamic observables, production runs of 1 ns each were carried out for all systems, with system configurations saved every 0.1 ps. All the analyses were performed over the last 0.5ns of the production run data.

MD simulations were performed under constant pressure and temperature conditions. Pressure was maintained at 1 atm using Langevin Piston [27]. Temperature coupling to external heat bath was used to maintain temperature at 305 K. Lennard-Jones interactions were smoothly truncated with cutoff 12 Å using switching function between 10 Å and 12 Å. Long-range electrostatic interactions were computed using particle mesh Ewald (PME) method. A timestep of 2 fs was used for all simulations.

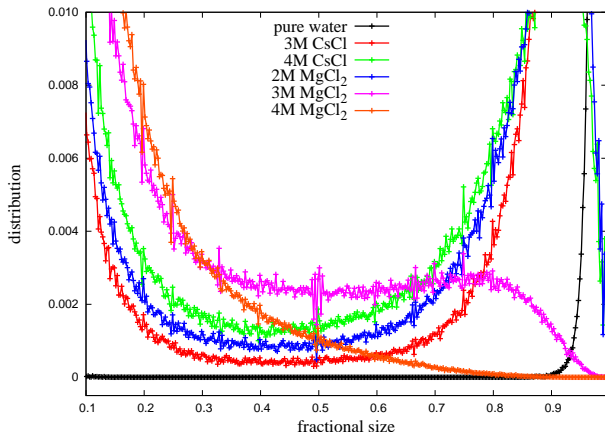


FIG. 1: Domain size distribution plots scaled to [0, 1] for all six systems considered in the study and for slab thickness of 4Å. The data is averaged over 50000 frames and 1 ns of simulation time.

*Water domain identification*– To identify hydrogen bond network domains in all the six systems considered in this study, each system was divided into multiple overlapping slabs along each of the three orthonormal directions. Over each such slab, hydrogen bonded domains of water molecules were identified. The criterion for inclusion of water molecules to a single domain is the existence of a bidirected path between every pair, via a network of hydrogen bonds formed by water molecules in the same slab. Using this definition of water domain, it was observed that for pure water all values of slab thickness  $\geq 2.7\text{\AA}$  consistently resulted in a single spanning domain along the slab. Addition of salt to the water systems resulted in formation of multiple water domains, even when higher values of slab thickness (4Å) were considered. The size distribution of different domains of water for a slab thickness of (4Å) and various concentrations of added salts, in comparison with the case of pure water is shown in FIG. 1. From the figure, it can be seen that for the case

of pure water, a single spanning domain exists. With the addition of  $\text{MgCl}_2$  salt, the size distribution of water domains depends on the concentration. For 2M salt concentration, the domain size distribution is similar to the pure water case, with additional appearance of smaller sized water domains. When the concentration of  $\text{MgCl}_2$  is increased to 3M and above, the domain size distribution differs significantly from that of pure water. No single spanning domain remains in the system and the system primarily consists of many domains of water of varying size distribution. Ion specific local structural effects on water has been widely studied in the literature [16, 28–32], generally classifying ions into structure-makers and structure-breakers [6, 32–34] based on their effect on the hydrogen bond network of water. High charge density ions have been known to exert strong patterning effects on first solvation shell water molecules leading to a reduction in water-water hydrogen bonding [35–37].

This is not the case with addition of CsCl salt to the water system. As can be seen from the figure, even at concentration of 4M, the domain size distribution is similar to the pure water system. In a recent ab initio MD study of water systems with NaCl and CsI [38], salts with low-charge density ions, similar spanning hydrogen bond networks were observed to exist. Following the identification of domains, water molecules residing at the domain boundaries were identified and recorded for all the three orthonormal directions. From this data, the water molecules which appear in all the three lists, corresponding to three orthonormal directions, are identified and labeled defect waters. This set of defect water molecules however may contain water molecules which are within the first hydration shell of any ions. From this super set of defect water molecules, a subset of water molecules which are not within the first hydration shell of any ion were identified, which are referred to henceforth as *waterD* (pure water is referred to as *waterP*). A further sub-population of defect water molecules were also identified: water molecules which are at domain boundaries in any two orthonormal directions (instead of three) and not in the first hydration shell of ions. These will be referred as *waterD2*.

*a. Results*– Reorientation autocorrelation functions  $P_1(t)$  and  $P_2(t)$  defined as first and second Legendre polynomials of water dipole vector ( $\vec{p}$ ), a unit bisector of the H-O-H angle, were computed for various sub-populations of water molecules over 20 ps:

$$P_1(t) = \langle \vec{p}(t) \cdot \vec{p}(0) \rangle \quad (1)$$

$$P_2(t) = \langle \frac{1}{2}(3\cos^2(\vec{p}(t) \cdot \vec{p}(0)) - 1) \rangle \quad (2)$$

where the angular brackets denote average over number of water molecules in each sub-population and time. The errors for  $P_1(t)$  and  $P_2(t)$  have been obtained by computing standard deviations using block averages. The computed correlation functions  $P_1(t)$  for pure water and  $\text{MgCl}_2$  solutions are plotted in FIG. 2 (plots of  $P_2(t)$  are given in FIG. SI and FIG. SII of *Supp. Info.*). A

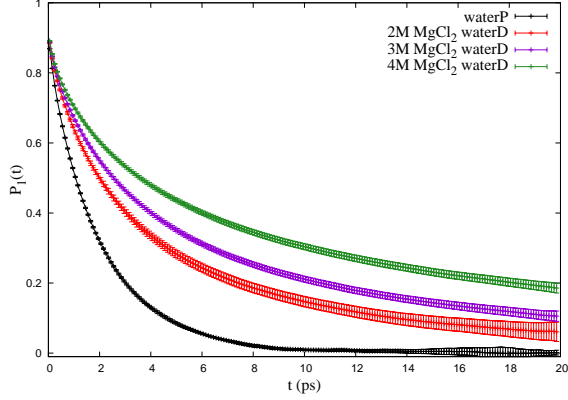


FIG. 2: Plots for  $P_1(t)$  for *waterD* in the presence of  $\text{MgCl}_2$  (colored curves) at the concentrations studied and pure water (black). The error bars in all plots have been magnified 5 times

significant slowing down of reorientational times for sub-population *waterD* as a function of salt concentration can be seen from the figure. These results suggest that ‘slow waters’ exist beyond the first hydration shell of both cations and anions. Earlier experiments and simulations show that the propensity of formation of ion-water clusters is higher at higher concentration of salts in water [39]. Water molecules trapped in such clusters can experience very slow reorientational times. It is to be noted that though the salt concentrations considered in this study are high, the sampling of sub-population *waterD* will not include such trapped waters, by definition. The *waterD* molecules considered can, at best, be part of three solvent separated ion pairs. Extensive studies of the reorientation of water molecules [40–44] have shown that autocorrelation functions of a body-set vector, including dipole vector, of water molecules involve distinct time scales. A fast, sub-picosecond decay due to librational motion followed by a slower component that can be attributed to structural changes such as hydrogen bond exchange and reorientations of hydrogen bonded water molecules. Multiexponential functions thus serve as good fit functions for such correlations and the correlations  $P_1(t)$  have been fit to either bi- ( $A_3 = 0$ ) or tri-exponential functions of the form  $P_1(t) = A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2}) + A_3 \exp(-\frac{t}{\tau_3})$  depending on the system. However, the attribution of specific physical processes to these time constants is not attempted in this work. A bi-exponential function ( $A_3 = 0$ ) was the best fit for  $P_1(t)$  curves for the pure water case. The decay time  $\tau_2 = 2.27$  ps agrees well with earlier results [45–47]. In the presence of  $\text{MgCl}_2$ , a tri-exponential function was found to be more appropriate, with dynamics of defect waters introducing a new time scale into the problem. The decay times ( $\tau_3$ ) are much larger than the slowest component of orientational relaxation for bulk water and show an increase with the concentration of  $\text{MgCl}_2$  salt. These results are shown in TABLE 1. Simulation results show that for the largest concentration

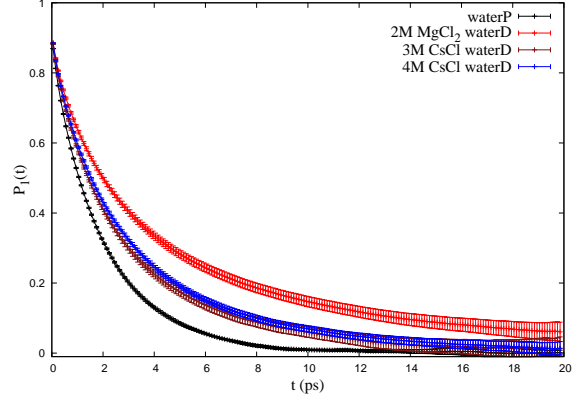


FIG. 3: Plots for  $P_1(t)$  for *waterD* comparing 3M and 4M  $\text{CsCl}$  with 2M  $\text{MgCl}_2$ . The black curve is for pure water. The error bars in all plots have been magnified 5 times

of  $\text{MgCl}_2$  studied (4M), the longest mode in decay time for defect waters, which are beyond first hydration shell of any ions, is as high as 22 ps. The  $P_1(t)$  curves for  $\text{CsCl}$  salt solutions are plotted in FIG. 3 and deviation from the case of pure water is much less significant compared to effects of  $\text{MgCl}_2$  and independent of salt concentration. The  $P_1(t)$  curves for  $\text{CsCl}$  are also fit with a tri-exponential function and the values are given in TABLE 1. The anion used in both the salts,  $\text{Cl}^-$ , is known to be weakly hydrated ion and such anions are expected to affect the dynamics of OH vector preferentially over dipole vectors of water molecule [9]. Thus the observed difference in reorientational dynamics between the two cations studied in this work,  $\text{Mg}^{2+}$  and  $\text{Cs}^+$  reflect the difference between a strongly hydrated vs a weakly hydrated cation, while both have the same counterion. Similar differences between  $\text{Mg}^{2+}$  and  $\text{Cs}^+$  are observed for the sub-population of water molecules *waterD2* as well and the results are included in *Supp. Info.* (FIG. SIII, FIG. SIV). These results seem to be consistent with the ordering of cations in well-known Hofmeister series [9].

Two dynamical quantities, which can be measured experimentally, related to ion hydration are the hydration number ( $N_{\bar{p}}$ ), defined as the number of moles of slow water dipoles per mole of dissolved salt and fraction of slow waters relative to bulk-like water ( $f_{\text{bulk}}^{\text{slow}}$ ) [8, 9]. The slow water molecules identified in the experiments are independent of structural definition of hydration shells and can contain water molecules within and outside the first hydration shells of ions. To be consistent with the experiments, a similar definition of slow waters was adopted which entails including water molecules in the first hydration shell of cations along with two sub-populations *waterD* and *waterD2*. Further, simulations allow a new dynamical quantity  $f_{(\text{bulk}, \text{defect})}^{\text{slow}}$  to be computed, which is difficult to measure experimentally.  $f_{(\text{bulk}, \text{defect})}^{\text{slow}}$  measures the fraction of slow waters beyond first hydration shell of ions relative to bulk-like water. The  $N_{\bar{p}}$ ,  $f_{\text{bulk}}^{\text{slow}}$  and  $f_{(\text{bulk}, \text{defect})}^{\text{slow}}$  for both  $\text{MgCl}_2$  and  $\text{CsCl}$  solutions are

salt	sub-population	$A_1$	$\tau_1$	$A_2$	$\tau_2$	$A_3$	$\tau_3$
none		0.127( $\pm 0.004$ )	0.588( $\pm 0.048$ )	0.761( $\pm 0.002$ )	2.272( $\pm 0.026$ )		
MgCl <sub>2</sub>	(2M, <i>waterD</i> )	0.071( $\pm 0.002$ )	0.439( $\pm 0.062$ )	0.464( $\pm 0.002$ )	2.446( $\pm 0.022$ )	0.355( $\pm 0.003$ )	10.731( $\pm 0.002$ )
	(3M, <i>waterD</i> )	0.078( $\pm 0.001$ )	0.463( $\pm 0.034$ )	0.424( $\pm 0.002$ )	2.846( $\pm 0.013$ )	0.388( $\pm 0.003$ )	14.957( $\pm 0.001$ )
	(4M, <i>waterD</i> )	0.088( $\pm 0.002$ )	0.561( $\pm 0.020$ )	0.347( $\pm 0.002$ )	3.280( $\pm 0.014$ )	0.452( $\pm 0.003$ )	22.081( $\pm 0.001$ )
CsCl	(3M, <i>waterD</i> )	0.049( $\pm 0.002$ )	0.204( $\pm 0.539$ )	0.455( $\pm 0.004$ )	1.671( $\pm 0.056$ )	0.404( $\pm 0.005$ )	5.110( $\pm 0.003$ )
	(4M, <i>waterD</i> )	0.067( $\pm 0.001$ )	0.428( $\pm 0.042$ )	0.512( $\pm 0.003$ )	2.160( $\pm 0.020$ )	0.315( $\pm 0.004$ )	6.250( $\pm 0.002$ )

TABLE I: Water reorientational time constants in absence of salt and for for (X, *waterD*) sub-populations obtained from tri-exponential fits. All time constants are in picoseconds.

given in TABLE II. It has been suggested that the typical hydration number,  $N_{\bar{p}}$ , for many ions is around 6 and any value greater than this number indicates presence of long-range effects of ions [8]. Experiments on salt solutions containing both strongly hydrated cations and anions show a large  $N_{\bar{p}}$  value of the order of 18 and this has been suggested as a strong indication of cooperative slow down of water dynamics beyond first hydration shells of such ions [8]. In the present study the  $N_{\bar{p}}$  values for MgCl<sub>2</sub> for all the three concentrations studied is 7, indicating the existence of the long-range effect of Mg<sup>2+</sup> ions in the presence of Cl<sup>-</sup>, albeit weaker than when the counterion is SO<sub>4</sub><sup>2-</sup>. The  $N_{\bar{p}}$  values for CsCl were found to be less than 6.

From TABLE II, it can also be seen that the fraction of slow waters relative to bulk-like water, beyond first hydration shell ( $f_{(\text{slow}, \text{defect})}$ ) for 2M MgCl<sub>2</sub> is only 0.02. This small value may suggest why long-range effects of strongly hydrated cations were not conclusively found in earlier simulations. A snap shot of MgCl<sub>2</sub>-water system for 2M salt concentration is shown in FIG. 4. The defect waters, which are beyond the first hydration shell of any ions are shown as van der Waals spheres and it can be seen that they form a small fraction of total number of water molecules in the system. Values of  $f_{\text{slow}, \text{bulk}}$  as a function of radial distance from cations was computed and are given in TABLE SII in *Supp. Info.*. Within 2.5 Å, a typical radial distance defining first hydration shell, the fraction of slow waters to bulk  $f_{\text{slow}, \text{bulk}}$  for 2M Mg Cl<sub>2</sub> concentration is 0.52. This value drops to 0.12 just above 3 Å and progressively decreases beyond first hydration shell. However the non-zero values of  $f_{\text{slow}, \text{bulk}}$  well beyond first and second hydrations shells of Mg<sup>2+</sup> ions even at 2M concentration indicate delocalised presence of slow waters. These results suggest that an oft-used definition of radially varying hydration shell definition of classifying water molecules may not be able to capture this small fraction of water molecules which are affected by the presence of ions and which are beyond first hydration shell. The definition of defect waters *waterD* used in this study can capture these small fraction of slow water molecules and suggest long-range effects of strongly hydrated cations such as Mg<sup>2+</sup>. It can also be seen from the TABLE II that this fraction of defect water molecules increases with concentration and a significant jump occurs in such fraction from 2M to 3M (0.02 to 0.35). This suggests that a

global network of defect waters may occur at higher salt concentrations. The values of  $f_{\text{slow}, \text{bulk}}$  and  $f_{(\text{slow}, \text{defect})}$  for CsCl salt solutions is very small, consistent with results in FIG. 3.

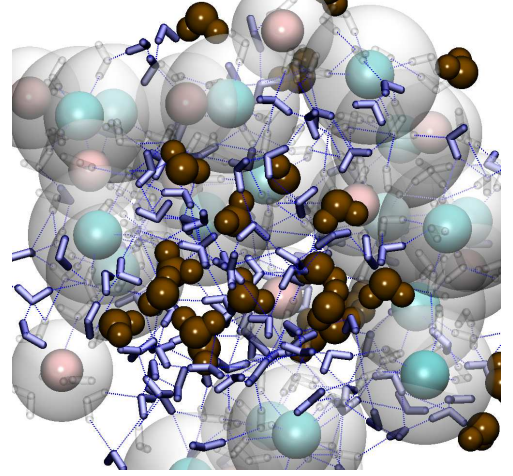


FIG. 4: Snapshot of part of MgCl<sub>2</sub>-water system at 2M salt concentration. The Mg<sup>2+</sup> and Cl<sup>-</sup> ions are shown as cyan and pink spheres. The first hydration shells (2.5 Å radius) around the ions are also shown as transparent spheres. The defect waters, *waterD*, which are not within the first hydration shell are shown in VDW representation in brown and the other water molecules are shown in stick representation (transparent for water molecules in the first solvation shell of ions). The hydrogen bond network among water molecules is also shown.

salt, conc.	$N_{\bar{p}}$	$f_{\text{slow}, \text{bulk}}$	$f_{(\text{slow}, \text{defect})}$
MgCl <sub>2</sub> , 2M	7.1	0.18	0.02
MgCl <sub>2</sub> , 3M	7.2	0.59	0.35
MgCl <sub>2</sub> , 4M	7.0	0.95	0.44
CsCl, 3M	5.7	0.04	0.02
CsCl, 4M	5.7	0.10	0.07

TABLE II: Approximate values of quantities  $N_{\bar{p}}$ ,  $f_{\text{slow}, \text{bulk}}$  and  $f_{(\text{slow}, \text{defect})}$  obtained. The data is averaged over 50000 frames and 1 ns of simulation time.

*Conclusion*– To summarize, MD simulation results in this study support the concentration dependent effects of strongly solvated ion species (Mg<sup>2+</sup>) on the reorientational dynamics of water molecules beyond the first hy-



dration shell. A likely mechanism for the same has been suggested in terms of salt induced propagating defects in the underlying hydrogen bond network of water which is in agreement with concepts of ion induced patterning of water at long distances. While the actual number of water molecules beyond ion hydration shells that exhibit slow reorientations is limited to a relatively small fraction of the overall number, especially at smaller concentrations, they have been observed to be distributed over network defects and over appreciably large spatial separations from the ions. The fractional number has been observed to increase monotonically with increase in the concentration of  $\text{MgCl}_2$ . It is to be noted that

the long-range effect of  $\text{Mg}^{2+}$  ions in the presence of a weakly hydrated counterion  $\text{Cl}^-$  is smaller than experimentally observed effects in the presence of  $\text{SO}_4^{2-}$  [8], but not insignificant. Possible reason for non-observance of the same effect in prior simulation works has been suggested through differences in selection of water molecules. Comparison with weakly solvated cationic species ( $\text{Cs}^+$ ) has been seen to be in agreement with the Hofmeister series. A non-polarizable force field was used for modeling water in the present study, and these results are expected to be enhanced when polarizable models of water are used and are a part of future studies.

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